On the Calculation of Results in Gas-Analyses.

By Samuel P. Sadtler, Ph.D.

At the last meeting of the Society I promised to present a full discussion of the formulas involved in calculating analyses of gaseous mixtures such as are found exhaling from the earth in the oil-regions of Western Pennsylvania and elsewhere. I am led to do this at present, chiefly because of some remarks made upon this subject by Prof. Henry Morton, in an article in the "American Gas-Light Journal" of Feb. 16th, 1878. Otherwise I should have deferred a discussion of the subject until I should have completed some absorption-tests upon the gases and analyses of portions of the gaseous mixtures withdrawn by such absorptions. This complete discussion of the subject I promised in a verbal communication made to the Society at its meeting on Sept. 21st last, mention of which is made on page 11 of No. 100 of the Proceedings.

In the article of Prof. Morton alluded to, he shows that the eudiometric combustion of a mixture of hydrocarbons of the Paraffin series cannot give results capable of being reckoned into percentage composition, and referring to my article published in the Proceedings, Vol. XVI, pp. 206 and 585, shows that an error in my formulas enabled me to get a "solution in appearance where no solution was possible."

This error in the formulas I had discovered myself in the Spring of 1877, and I had the absorption tests which I had described at the meeting of Sept. 21st last made purposely to enable me to solve the question of the composition of the gases independently of the use of formulas. In a private letter to Prof. Morton, dated Dec. 31st last, in answer to one received from him a day or two before, calling my attention to the error, I acknowledged the error of the formula used by me in my printed paper, and mentioned that I was proposing to rectify the results as first published by the aid of other tests.

With reference to the matter of the impossibility of determining the composition of a mixture of gases belonging to the Paraffin or marsh-gas series, Prof. Morton shows very clearly in his paper that this impossibility does exist when we take three or more paraffins or a mixture of hydrogen and two or more paraffins. In this latter case the hydrogen molecule simply acts like a member of the series lower than marsh-gas or CH_4.

When we ask the question with reference to two members of this series, however, we find that a solution is not impossible. In reckoning the results of analyses of ordinary illuminating gas, it is always necessary to calculate the relative amounts of hydrogen and marsh-gas from the results of the eudiometric combustion, and what is true of marsh-gas and hydrogen (which latter we have just said must in such cases be considered as a lower member of the marsh-gas series) is true of marsh-gas and ethyl-hydride or marsh-gas and propyl-hydride. So we may, in dealing with the mixture of gases which has been submitted to a eudiometric combustion, and which we know by previous tests and absorptions cannot contain anything else

than hydrogen and the members of the Paraffin series, assume as the basis of our reckoning hydrogen and any member of the Paraffin series or marsh-gas and any single higher member of the same series. Several of these possible assumptions are alluded to in my paper read February 18th, 1876, found in No. 97 Proceedings, p. 210, and reasons given why they were then rejected as not applicable.

The reason why I was led into adopting the formulas used at that time are also given in the same connection. I made an error in the equation chosen to represent the contraction ensuing from the endiometric combustion, taking $3x + 2y + \frac{3}{2}z = A$, instead of $\frac{3}{2}x + 2y + \frac{3}{2}z = A$., where x $=$ hydrogen, $y =$ marsh-gas, $z =$ ethyl-hydride and $A =$ the observed contraction in volume of the gaseous mixture after the passage of the spark. I had used in reckoning the contraction of hydrogen the atom H instead of the free molecule H_2. As stated (loc. cit.) I found in Fougué's memoirs a confirmation of my results. The same error had evidently existed in his mind, although it did not show as plainly, as he published no percentage results. After giving equations to be used on the supposition of a mixture of marsh-gas, ethyl-hydride, and propyl-hydride, he says:
"Tout mélange de carbures d'hydrogène de la formule $c^n H^{2n} + 2$ doit remplir la condition exprimée par cette dernière equation, c'est à-dire que le volume de l'acide carbonique formé dans l'eudiomètre par combustion doit être éqal á deux fois l'absorption produite moins trois fois le volume du gaz. Le mélange de ces carbures avec l'hydrogène libre ou avec d'autres carbures d'hydrogène empêche cette condition d'être realisée. Il est donc facile des reconnaitre si un mélange de carbures d'hydrogène gazeux contient exclusivement des carbures de formule $c^{2n} H^{2n} - 2$."—*Compt. Rend.* Vol. 87, p. 1048.

Finding in the combustion results of all the analyses reported upon in my first paper an excess of contraction over that required by Fougué's law just stated above, I ascribed it (as he did in theory) to the presence of hydrogen. I felt sure that I had sufficient knowledge of the details of the manipulation and of the errors to be avoided there, to put out of the question the idea that this excess of contraction might be owing to having passed the spark with an insufficient supply of diluting air present with the explosive mixture in the eudiometer. The contraction was proportionally great too in parallel analyses of the same gas.

I recognized, as before stated, shortly after the publication of the second paper, the error in the formula expressing the contraction, and saw that while the qualitative tests described in my first paper showed the presence of ethyl and propyl-hydrides, the quantitative results based upon a wrong formula would have to be revised.

Before publishing my final revision of them, I desired to verify in the fullest way my qualitative absorption results before published, and to obtain, by the aid of these absorptions, material better adapted to give satisfactory quantitative results. This work, though unavoidably interrupted and delayed, I have now in hand. Without giving at present any final revision to my published analyses, I feel obliged to notice a criticism made

475

upon them in Prof. Morton's article above referred to. After stating that no solution of the problem of analysing a mixture of three members of the Paraffin series, or of hydrogen and two members of the same series was possible, Prof. Morton concludes by saying, with reference to my analyses, "and his determinations have therefore no value whatever."

In reply to this, I would say that, while, in view of the demonstration made by Prof. Morton in his paper, which was by the way fully accepted by me before I saw it in his article, I am unable to accomplish all that I first thought I could, my figures are still of *some* account. They possess just the same value and can be used in just the same way as the figures obtained by any analyist in making an analysis of ordinary illuminating gas.

As shown in the first part of this paper, we are able to determine from the combustion results, the proportions in a mixture considered as made up of two members of the Paraffin series or of hydrogen and one member of the series. That this can be done with a gas known to contain the higher Paraffins along with marsh-gas, is shown in Prof. Morton's own analysis of a water-gas in which he had proved these Paraffins to be present (loc. cit.). It is shown in the analysis of Prof. Morley of the natural gas from the Neff. Well. Ohio, quoted in my second paper (loc. cit.).

My results then can be reckoned in this way, and the gaseous mixture which is submitted to the eudiometric combustion can be figured as made up of hydrogen and marsh-gas, or of marsh-gas and ethyl-hydride, as is more reasonable in all these cases. Here, however, hydrogen is not necessarily excluded, for part of what is reckoned as marsh-gas may be a mixture of equal parts of hydrogen and ethyl-hydride, and what is reckoned as this latter may be only that amount which is in excess of the hydrogen present.

Thus, in my first paper, I gave as present in the gas of the Burns Well 6.10% hydrogen, 75.44% marsh-gas, and 18.12% ethyl-hydride. If I calculate the combustion results (using the carbonic acid formed) given on p. 211 Proceedings No. 97, for marsh-gas and ethyl-hydride, I get as the average of the two analyses 87.66% marsh-gas and 12.00% ethyl-hydride. Now if this latter number 12.00% be taken from the 18.12% reckoned before, we have 6.12%, which combining with the 6.10% of supposed hydrogen would increase the 75.44% of marsh-gas to 87.66% of marsh-gas.

In the Erie gas, where only a trace of hydrogen was assumed before to be present, I can reckon the combustion results, using both the carbonic acid formed and the contraction ensuing on the combustion, and get results which do not differ greatly from those already published. Thus I gave before .43% hydrogen, 40.33% marsh-gas, and 58.26 ethyl-hydride. Calculated for the two latter constituents only, I get 40.53% marsh-gas and 58.49% ethyl-hydride.

I do not propose, however, to give these or any results as final until I have finished the examination of the gases which I had absorbed with different reagents and of various decomposition products obtained from them. I hope then to be able to establish with some certainty the exact character of the natural gases which I have made the subject of study.

University of Penna., *April 5th*, 1878.